Phase composition distribution simulation of titanium oxide nanosize structures obtained by the local anodic oxidation method

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Nanostructures controlled formation is one of the most important tasks of modern nanotechnology. This task is particularly relevant for the memristor structures formation, since their characteristics are influenced not only by the geometric dimensions, but also by the phase composition distribution in the oxide nanosize structure volume, which is the basis for the memristor manufacture [1]. Therefore, the purpose of this work is to develop a mathematical model that allows to calculate the phase composition distribution in the oxide nanosize structure volume obtained by the local anodic oxidation method using a scanning probe microscope.

Modeling the phase composition of oxide nanosize structures obtained by the metal local anodic oxidation method a is a multi-step process and involves the generation of oxygen ions in humid air due to the decomposition of water molecules under the influence of an external electric field; oxygen ions mass transfer from the air into the oxide volume and to the metal-oxide boundary; an increase in the oxide volume in the metal oxidation process; metal oxide phase transitions due to the supply of an additional oxidizing agent to the previously formed oxide volume.

Thus, to solve the problem, it is necessary to solve the system of differential equations:

$$\begin{cases} \nabla(\varepsilon\varepsilon_0\nabla\varphi) = -\rho(N) \\ \nabla(-\mu N\nabla\varphi + D\nabla N) = R(\varphi) \end{cases},$$

where φ and N are electric potential and oxygen vacancies distribution in the oxide volume, $\varepsilon\varepsilon_0$ is the medium dielectric constant, $\rho(N)$ is the oxygen ions volume charge density, μ and D are oxygen ions mobility and diffusion coefficient, $R(\varphi)$ is the generation rate oxygen ions in the air.

The joint solution of the presented system of equations will allow one to obtain the oxygen ions distribution in the oxide volume and the oxygen ions flow to the surface. The obtained results are necessary for calculating the phase transitions in the oxide and the oxide growth rate during local anodic oxidation.

On the basis of the developed model, a numerical simulation of the LAO titanium film process was carried out using the MATLAB application software package using the *Partial differential equation* module algorithms, which allows solving systems of nonlinear differential equations in partial derivatives. For this, the electrochemical cell geometry was considered, including an AFM probe, an air medium, an oxide, and a metal film, for which the solution of a given differential equations system was found. Then, the oxygen ion flux distribution over the metal surface and the oxide growth rate were determined, and phase transitions in the oxide volume were calculated.

As a result, the distributions of the TiO, Ti_2O_3 and TiO_2 phases were obtained (Fig. 1), the analysis of which showed that the TiO phase forms near the oxide-metal interface, the Ti_2O_3 phase is in the oxide volume, and the TiO_2 phase is present near the oxide surface. The results obtained can be explained by the fact that in the process of LAO diffusion of oxygen ions takes place through the oxide layer to the metal surface and, accordingly, the ion concentration decreases from the air medium to the metal. Thus, under conditions of oxygen lack, the TiO phase is formed, and under conditions of high oxygen concentration, the oxide is oxidized to TiO_2.

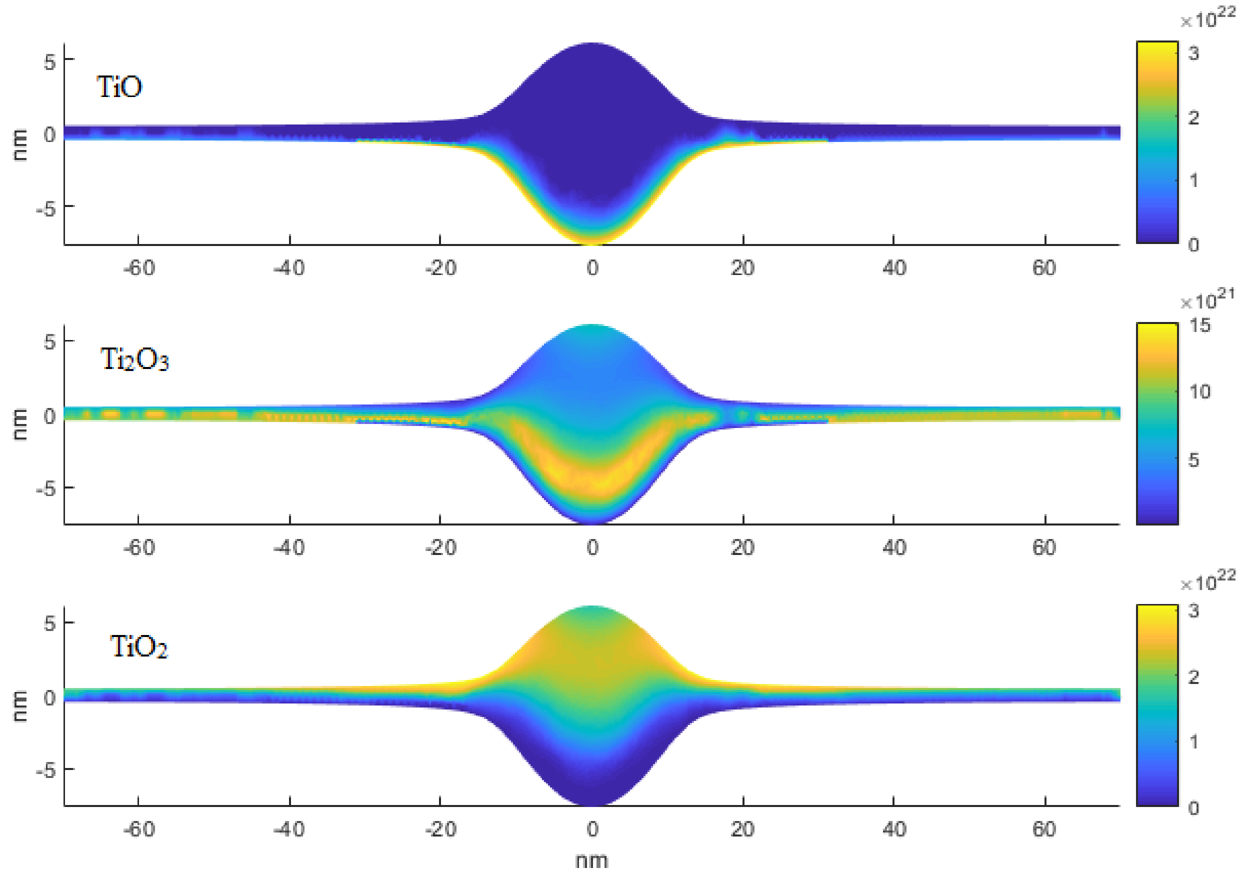

Figure 1. The titanium oxide phases concentration in the volume of the oxide nanosize structure formed by the local anodic oxidation method

The results obtained correlate well with the experimental results of titanium oxide nanosize structures phase composition XPS analysis on the surface and by ion etching into the oxide [2].

The obtained results can be used in the development of technological processes for the fabrication of the RRAM element base based on titanium oxide nanostructures.

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